



2014 EUVL Symposium, Oct 27-29, Washington DC.

Accelerating the next technology revolution

# Novel patterning materials research at SEMATECH: current status and future outlook

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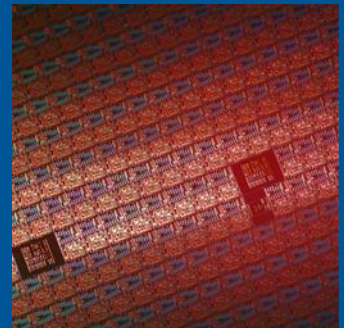
Mike Lercel, SEMATECH

Robert Brainard, CNSE

Christopher Ober, Cornell University

Souvik Chakrabarty, Cornell University

Daniel A. Freedman, SUNY, New Paltz





# Introduction



- EUV and high volume manufacturing
- SEMATECH novel resist programs:
  - Nanoparticle resist
  - Molecular organometallic resist
  - Negative tone resist ( focus of another talk)
- Path towards volume manufacturing
- Summary



# Pathfinding to HVM



## 1. Pathfinding:

1. New materials system
2. Understanding mechanism
3. most of university research

## 2. Pre-Development/Development

- I. Process parameters/properties: Outgassing/shelf-life
- II. Manufacturing compatibility

## 3. Enable the supply chain for early adoption



# High volume manufacturing



Transistor  
density/clock  
speed: high  
resolution

Timing  
matching:  
low LER

Tool  
compatibility  
contamination  
: outgassing/  
metal  
contamination

High  
throughput:  
low dose

Logistics  
complexity:  
Shelf life

Environme  
ntal /  
Health  
effect



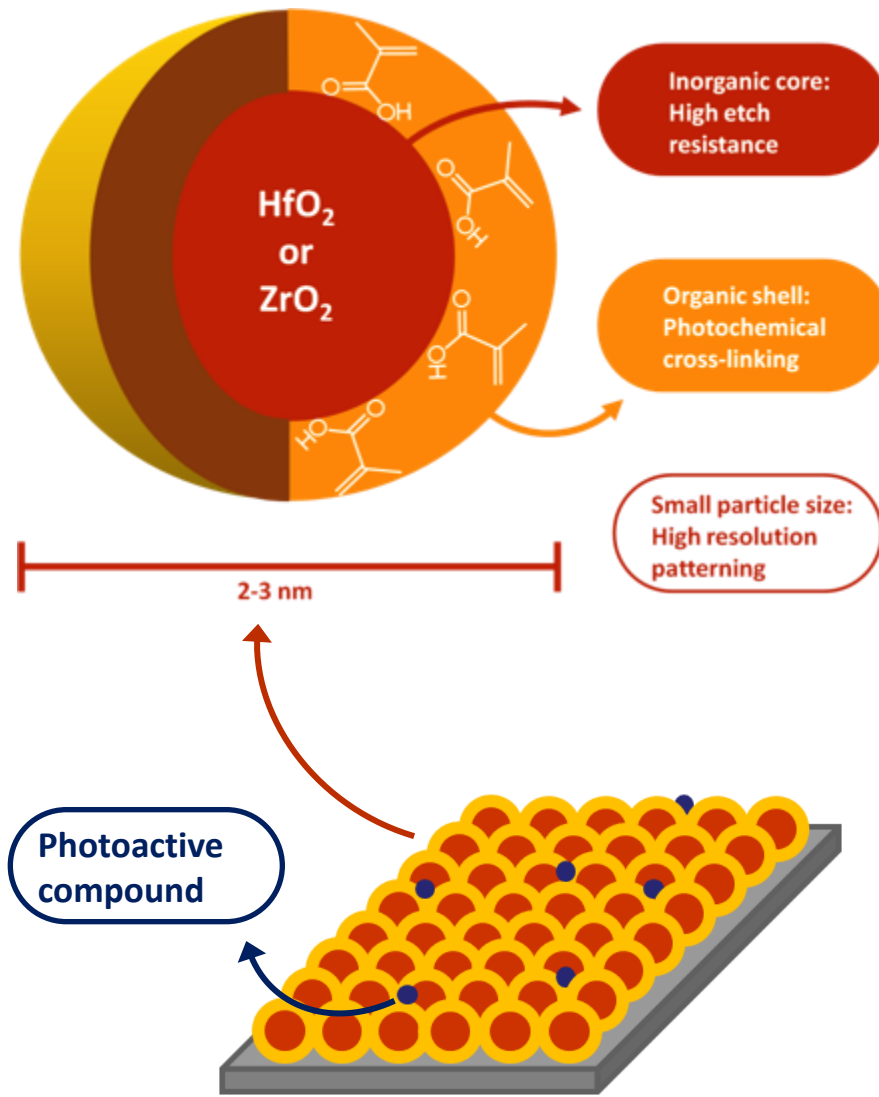
# Why nanoparticle resists



- High sensitivity to EUV dose (1-3mJ/cm<sup>2</sup>, compared to 20 mJ/cm<sup>2</sup> or higher for conventional EUV resists).
  - This is important particularly since there are still challenges associated with having a sufficiently high power EUV source
- The etch selectivity of these materials are high ( almost 10:1) due to metal content.
  - This enables migration to thinner resist and therefore potentially higher resolution.
- SEMATECH and Cornell is scaling up batches of few baseline resists to study batch-to-batch variations and self-life
- SEMATECH is also engaged in studying EHS characteristics of this resist system ( with University of Arizona).



# Nanoparticle resist



## Hybrid organic/inorganic nanoparticles:

Metal oxide with organic surface ligands

### Inorganic core:

ZrO<sub>2</sub> or HfO<sub>2</sub>, other metal oxides can be used.

### Ligand Surface:

Carboxylate, phosphonate and sulfate studied to date

### Photoactive Compounds:

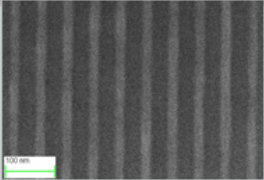
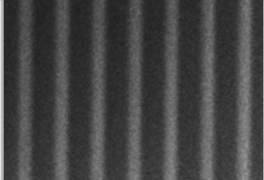
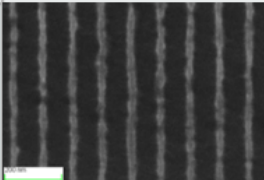
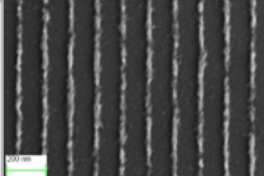
Either PAG or photoradical generator

**NOT CHEMICALLY AMPLIFIED**




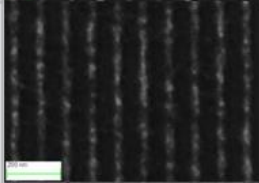
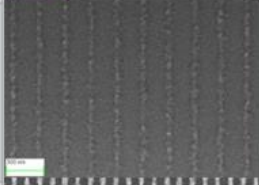
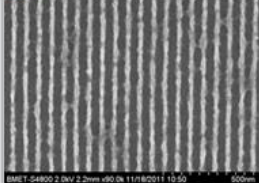
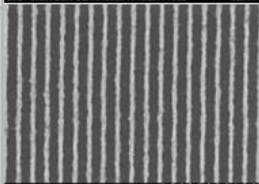
# Nanoparticle resist ( pathfinding)

- Work carried out in Cornell University
- High dose sensitivity (~3-4 mJ) resist system developed

| materials                                     | Dose(mJ/cm <sup>2</sup> ) | Best resolution (CD and pitch) nm | LER(nm) | Image   | comments                      |
|---|---------------------------|-----------------------------------|---------|---|-------------------------------|
| HfO <sub>2</sub> -Benzoate (7% non-ionic PAG) | 15                        | 22 (1:1)                          | 3.4     |    | O-Xylene developer            |
| ZrO <sub>2</sub> -benzoate (3% non-ionic PAG) | 20                        | 34 (1:2)                          | 4.7     |    | O-Xylene developer            |
| HfO <sub>2</sub> -DMA (5 wt% non-ionic PAG)   | 2.2                       | 20 (1:3)                          | 6.1     |   | 4-methyl 2-pentanol developer |
| ZrO <sub>2</sub> -DMA (5 wt% non-ionic PAG)   | 1.4                       | 20 (1:3)                          | 6.6     |  | 4-methyl 2-pentanol developer |



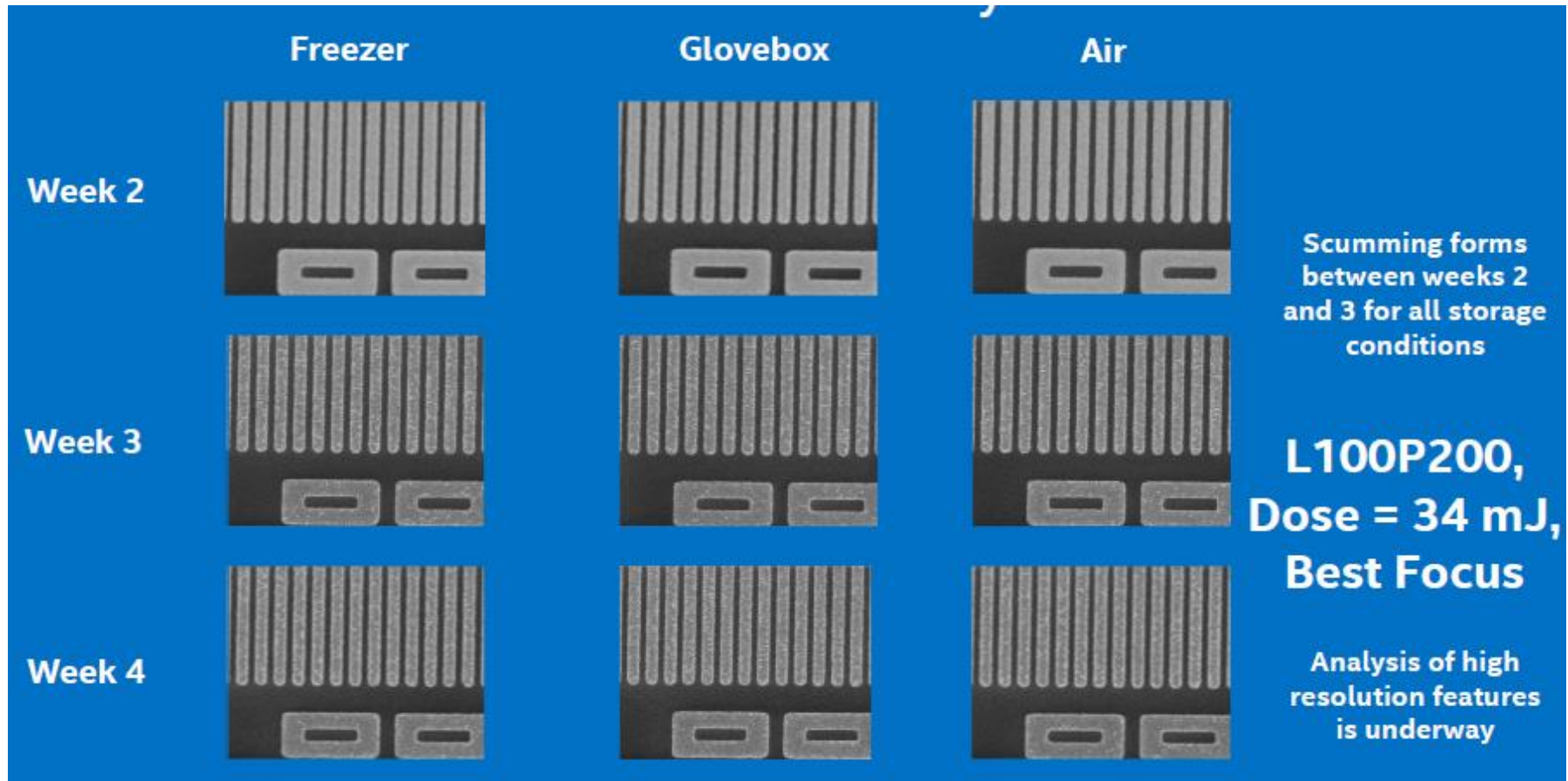
# Nanoparticle resist system

| materials   | Dose(mJ/cm <sup>2</sup> ) | Best resolution (CD and pitch) nm | LER(nm) | Image   | comments                      |
|---|---------------------------|-----------------------------------|---------|---|-------------------------------|
| Blend 1:<br>ZrO <sub>2</sub> -MAA : ZrO <sub>2</sub> -DMA | 2                         | 26 (1:3)                          | 6.0     |    | 4-methyl 2-pentanol developer |
| Blend 2:<br>ZrO <sub>2</sub> -MAA : HfO <sub>2</sub> -DMA | 2                         | 26 (1:3)                          | 7.5     |    | 4-methyl 2-pentanol developer |
| ZrO <sub>2</sub> -IBA (5 wt% non-ionic PAG)               | 2.6                       | 30 (1:4)                          | 6.9     |    | 4-methyl 2-pentanol developer |
| ZrO <sub>2</sub> -MAA (5 wt% non-ionic PAG)               | 4.2                       | 22 (1:1)                          | 5.6     |   | 4-methyl 2-pentanol developer |
| HfO <sub>2</sub> -MAA (5 wt% non-ionic PAG)               | 4.2                       | 24 (1:2)                          | 4.9     |  | 4-methyl 2-pentanol developer |



# Nanoparticle resist: shelf-life

- Shelf life study: scumming between weeks 2 and 3: only particle aging studies: could be better for solution

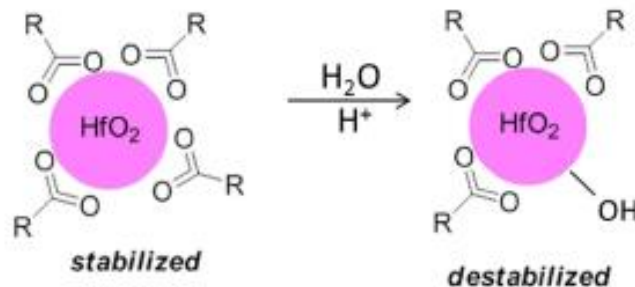


Courtesy: Marie Krysak, Intel Corp.

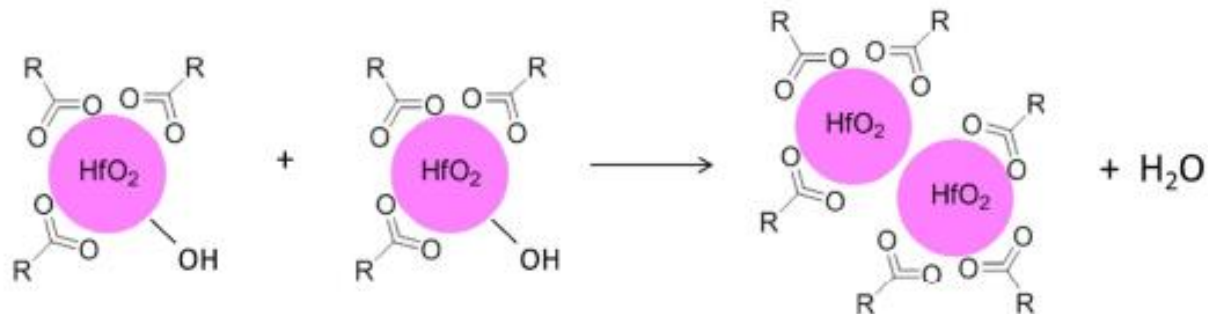


# Powder aging model for nanoparticles

## 1) Hydrolysis in the presence of water, acid



## 2) Condensation of neighboring destabilized particles leads to larger, insoluble particles responsible for scumming



Courtesy: Marie Krysak, Intel Corp.



# Shelf life (Cornell)



- Resist solution
  - Exposed after 10 days and 45 days.
  - Loss of sensitivity, ranging from 5 mJ/cm<sup>2</sup> to 15 mJ/cm<sup>2</sup> in 6 weeks
  - Upper limit: but needs finer time scale.



# EHS study of nanoparticles



- **Cytotoxicity**

- Aerobic respiration testing
- Anaerobic methanogenic test
- Microtox assay
- Real time cell analysis

**Microorganisms**

**Human cells**

**Nanoresist colloidal stability** in bioassay medium

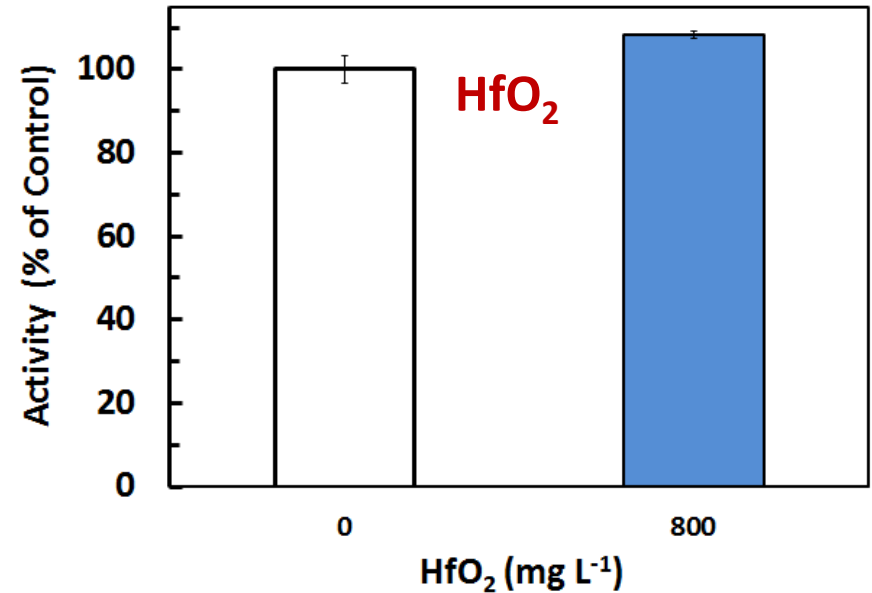
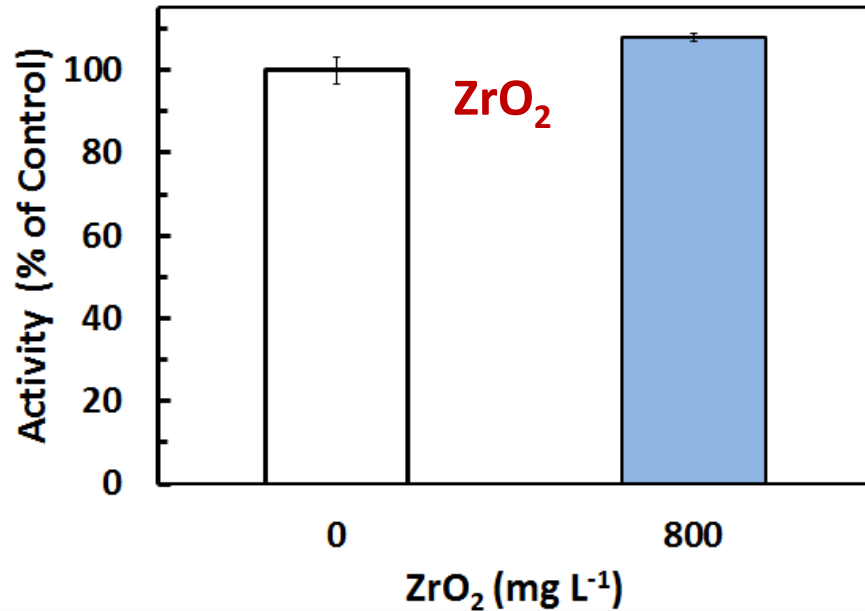
- Particle size distribution and zeta potential

**Release of soluble ligand from NP suspensions**  
in bioassay medium

Data: Reyes Sierra , Univ of Arizona



# Ligandless $\text{ZrO}_2$ and $\text{HfO}_2$ NPs: SEMATECH Methanogenic Toxicity Bioassays



- Ligandless  $\text{ZrO}_2$  and  $\text{HfO}_2$  nanoparticles didn't display microbial inhibition in aerobic and anaerobic bioassays at relatively high concentrations (up to 1200 mg NPs/L)
- The nano-photoresists showed different inhibitory responses in the Microtox bioassay.



# Outgassing study of nanoparticles



- Outgassing study ongoing( at IMEC)
- First indication is encouraging: comprehensive data next week.





# Full Field exposure

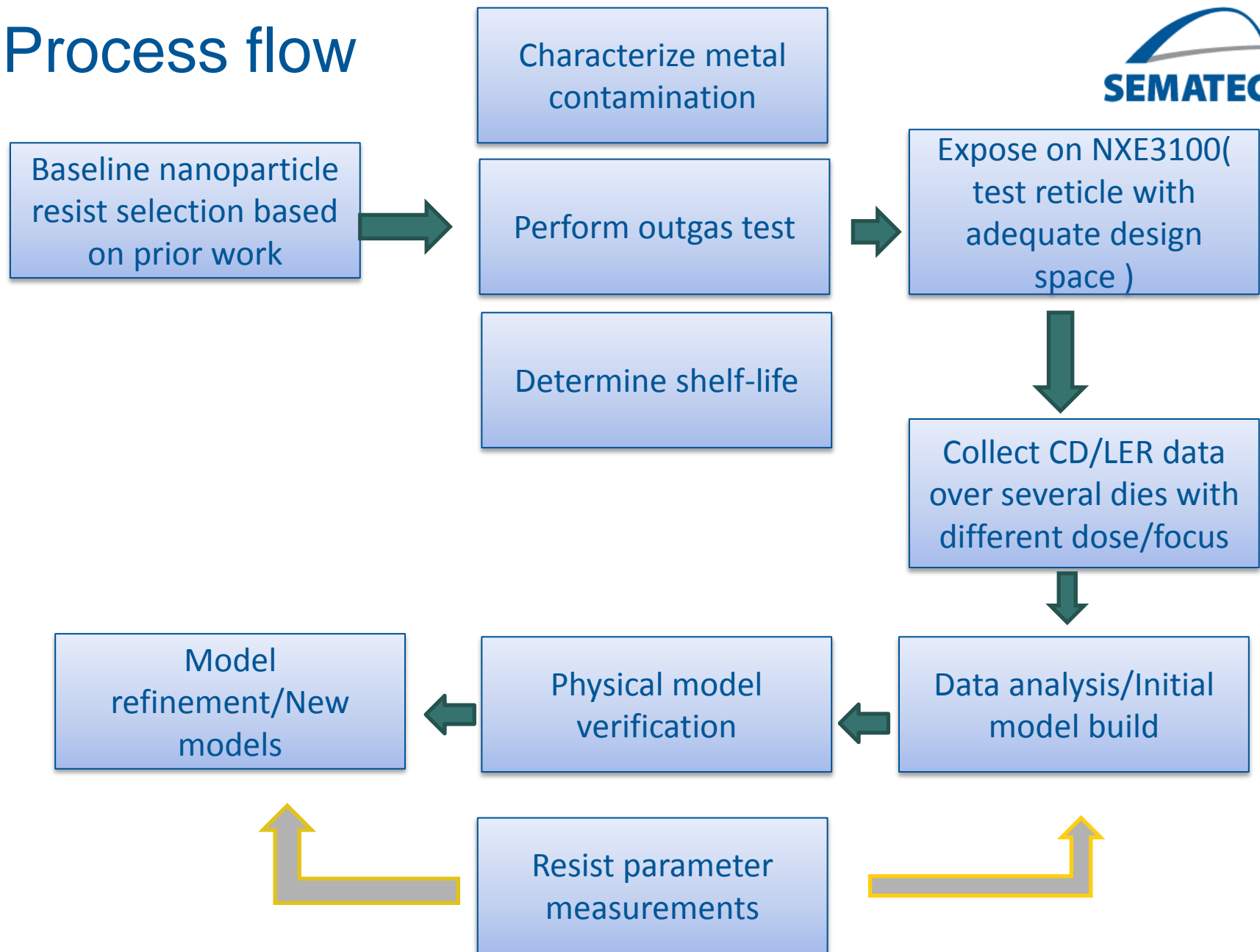


- So far system exposed on Microexposure Tool(MET)
- Necessary to expose on a HVM platform such as NXE
  - understand resist patterning mechanism in order to accelerate the HUV insertion timeline
- Exposure on NXE 3100 is being planned ( in cooperation with IMEC)
  - Metal contamination study using ICP is done:
    - Contamination in the order of 100ppb is observed for NA, Cd, Hf. Rest are below 10 ppb
  - Outgas testing conducted ( at IMEC)
  - Process window data
  - Build physical resist model
  - Batches of 100 ml samples are prepared for exposure on NXE 3100





# Process flow





# Molecular Organometallic EUV resist



# MORE project



- Three years of work under SEMATECH /Intel sponsorship:
  - approximately 500 different compositions characterized.
- Synthesized and evaluated ~500 compounds for:
  - Coating quality
  - EUV sensitivity
  - Imaging characteristics
  - Evaluated compounds containing: Cr, Co, Fe, Cu, Ni, Sn, Bi, Te, Sb
- Successes:
  - Several compounds capable of 18-nm resolution
    - High dose sensitivity : ~6mJ
    - Low LER: ~<2nm
  - Identified trends to assist in further improvements.
  - Progress is being made towards outgas testing and shelf-life optimization
- Critical for supply chain to adopt the technology.



# Molecular Organometallic Resists for EUV (MORE)



As EUV resolution improves, resists will be thinner. Traditional elements will no longer be able to stop enough EUV light for good photon statistics. Therefore, we are investigating elements in the periodic table with high EUV OD.

**We hope to Share Advantages of the Inpria/Cornell HfO<sub>2</sub> Resists:**

- High EUV OD.
- High stopping power of secondary electrons (less electron blur).
- Excellent etch resistance.

**We hope:** to have better control of performance by using a broader range of materials.

**To date, we have synthesized and screened ~500 organometallic compounds.**

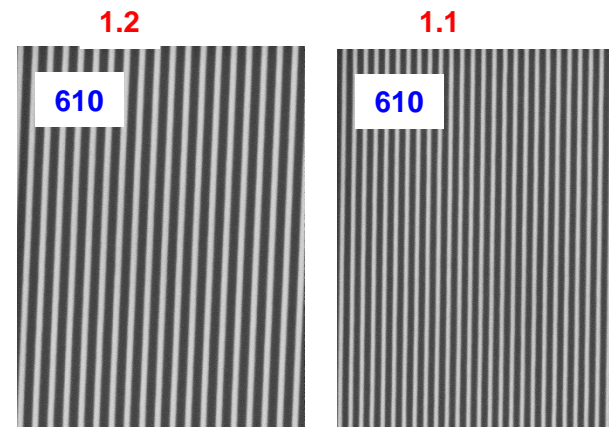
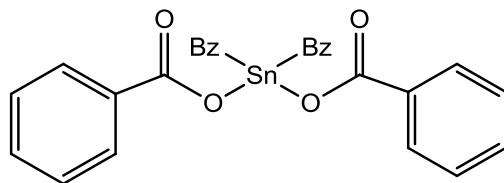
|                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |                |                |                 |          |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|----------------|----------------|-----------------|----------|
| 2.1<br>1<br>H   |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 | 2<br>He         |                |                |                 |          |
| 1.0<br>3<br>Li  | 1.5<br>4<br>Be  |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 | 2.0<br>5<br>B   | 2.5<br>6<br>C   | 3.0<br>7<br>N  | 3.5<br>8<br>O  | 4.0<br>9<br>F   | 10<br>Ne |
| 0.9<br>11<br>Na | 1.2<br>12<br>Mg |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 | 1.5<br>13<br>Al | 1.8<br>14<br>Si | 2.1<br>15<br>P | 2.5<br>16<br>S | 3.0<br>17<br>Cl | 18<br>Ar |
| 0.8<br>19<br>K  | 1.0<br>20<br>Ca | 1.3<br>21<br>Sc | 1.5<br>22<br>Ti | 1.6<br>23<br>V  | 1.6<br>24<br>Cr | 1.5<br>25<br>Mn | 1.8<br>26<br>Fe | 1.8<br>27<br>Co | 1.8<br>28<br>Ni | 1.9<br>29<br>Cu | 1.6<br>30<br>Zn | 1.6<br>31<br>Ga | 1.8<br>32<br>Ge | 2.0<br>33<br>As | 2.4<br>34<br>Se | 2.8<br>35<br>Br | 36<br>Kr        |                |                |                 |          |
| 0.8<br>37<br>Rb | 1.0<br>38<br>Sr | 1.3<br>39<br>Y  | 1.4<br>40<br>Zr | 1.6<br>41<br>Nb | 1.8<br>42<br>Mo | 2.2<br>43<br>Tc | 2.2<br>44<br>Ru | 2.2<br>45<br>Rh | 2.2<br>46<br>Pd | 1.9<br>47<br>Ag | 1.7<br>48<br>Cd | 1.7<br>49<br>In | 1.8<br>50<br>Sn | 1.9<br>51<br>Sb | 2.1<br>52<br>Te | 2.5<br>53<br>I  | 54<br>Xe        |                |                |                 |          |
| 0.7<br>55<br>Cs | 0.9<br>56<br>Ba | 1.1<br>57<br>La | 1.3<br>72<br>Hf | 1.5<br>73<br>Ta | 1.7<br>74<br>W  | 1.9<br>75<br>Re | 2.2<br>76<br>Os | 2.2<br>77<br>Ir | 2.2<br>78<br>Pt | 2.4<br>79<br>Au | 1.9<br>80<br>Hg | 1.8<br>81<br>Tl | 1.8<br>82<br>Pb | 1.9<br>83<br>Bi | 2.0<br>84<br>Po | 2.2<br>85<br>At | 86<br>Rn        |                |                |                 |          |

| EUV OD at Std. State Density<br>(Relative to Carbon) |     |     |     |      |       |
|--|-----|-----|-----|------|-------|
| 0-2  | 2-4 | 4-6 | 6-8 | 8-10 | 10-12 |



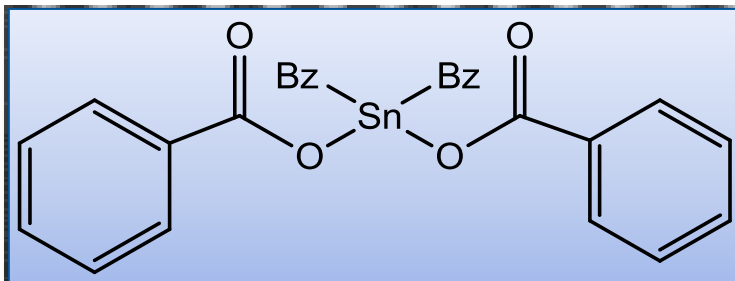
# MORE

- High speed group: dose 6-9 mJ/cm<sup>2</sup>: Sb-based
- Low LER compound: < 2nm, Sn-based



- Positive tone Pd/Pt group:
- Oxalate ligand group:
  - Focus of this talk





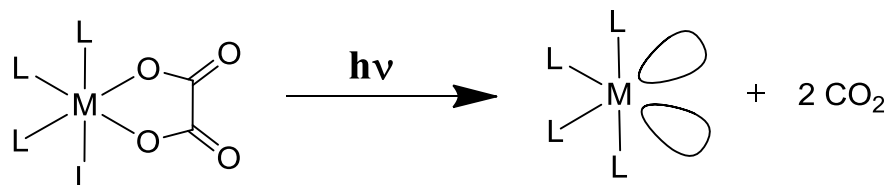
**1.1 nm LER\***

**610mJ**



## IV. Focus on Oxalate Complexes

Metal oxalates have a well-characterized photochemistry, resulting in a loss of  $\text{CO}_2$  and opening two binding sites for cross-linking.



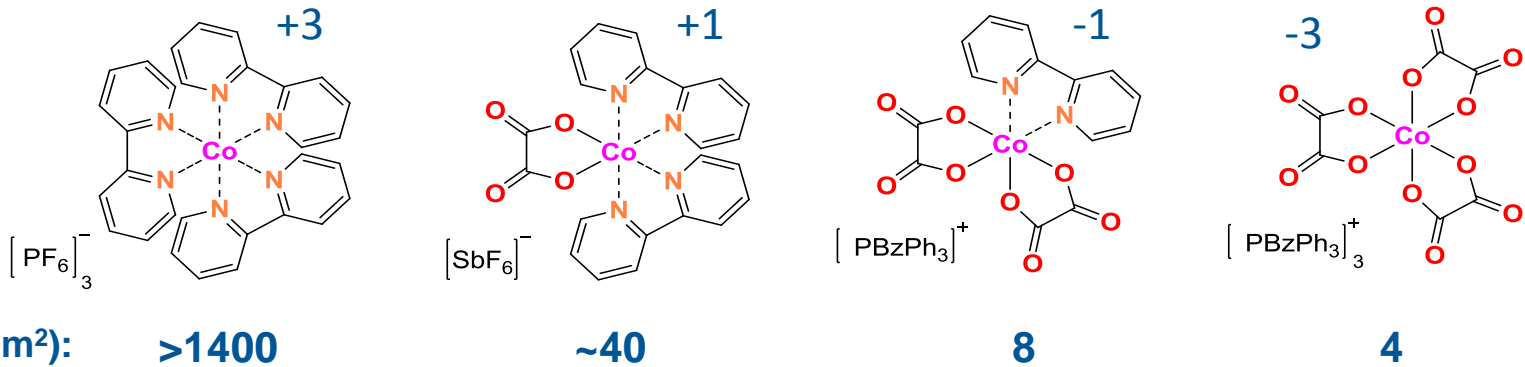
We have prepared 30 different oxalate complexes for testing which allows us to systematically explore variables such as:

- Central metal
- Oxalate loading
- Bipyridine vs. acetylacetonate vs. glycine



# IV. Oxalate Trends

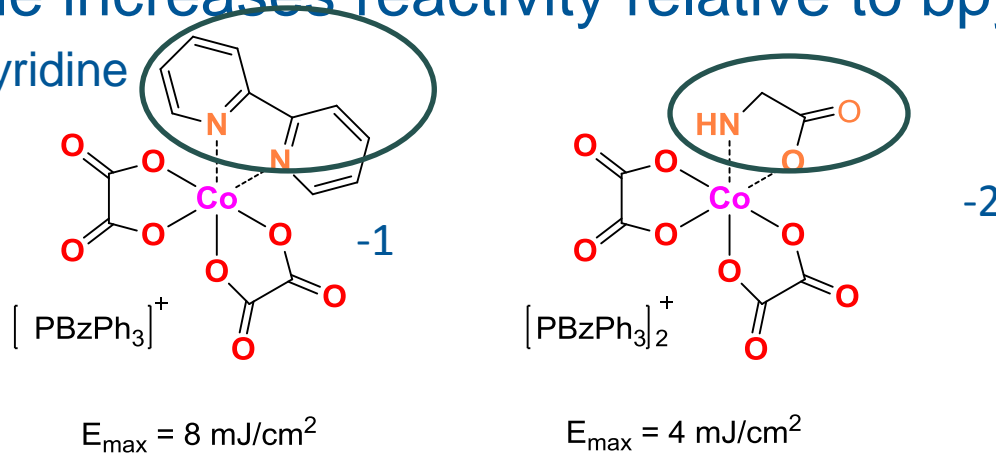
Trend #1: More oxalate, more negative the complex = faster resist



Trend #2:  $Co \geq Fe > Cr$

Trend #3: Glycine increases reactivity relative to bpy

Bipyridine





# IV. Imaging with Oxalate Compounds

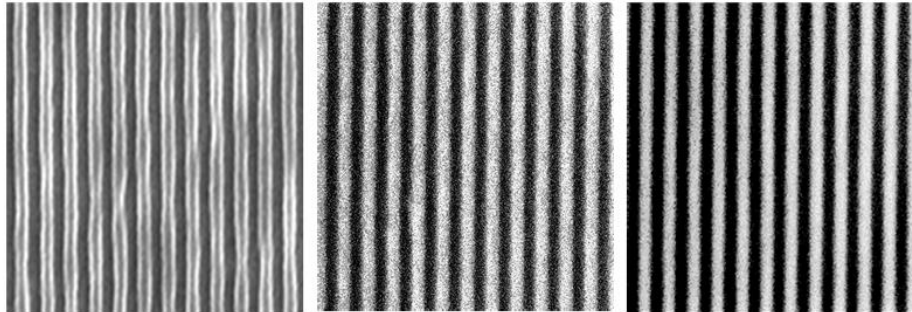
Central  
Metal (M):

Cr

Fe

Co

35 nm h/p  
lines:

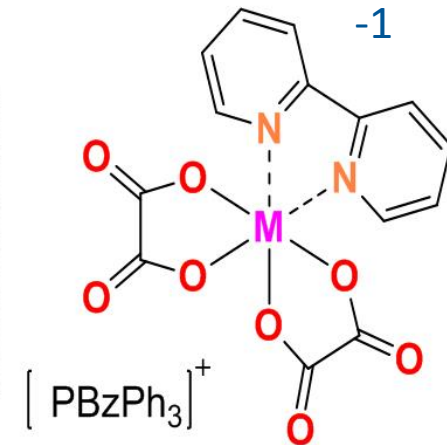


$E_{\text{size}}$   
(mJ/cm<sup>2</sup>):

70

48

27

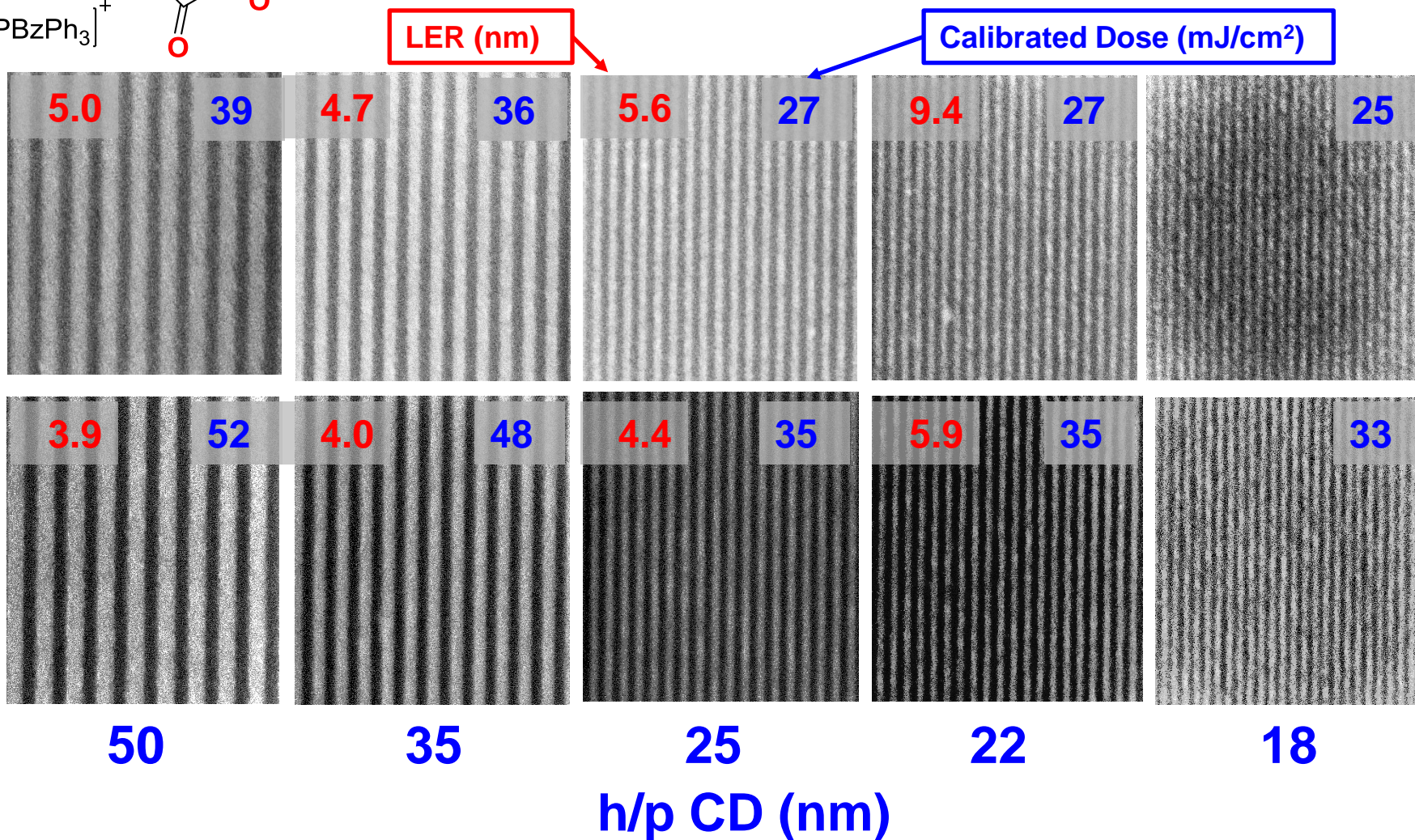
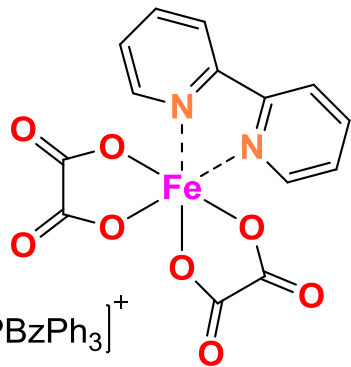


- Best results were with 2 oxalates and 1 bipyridine.
- Compounds with <2 oxalates are too slow.
- $M(\text{oxalate})_3$  complexes appear to be too reactive.

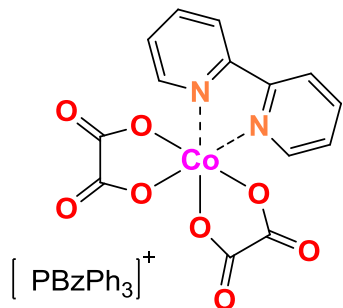


# Iron - Imaging at PSI SEMATECH

MEK Develop / 30s



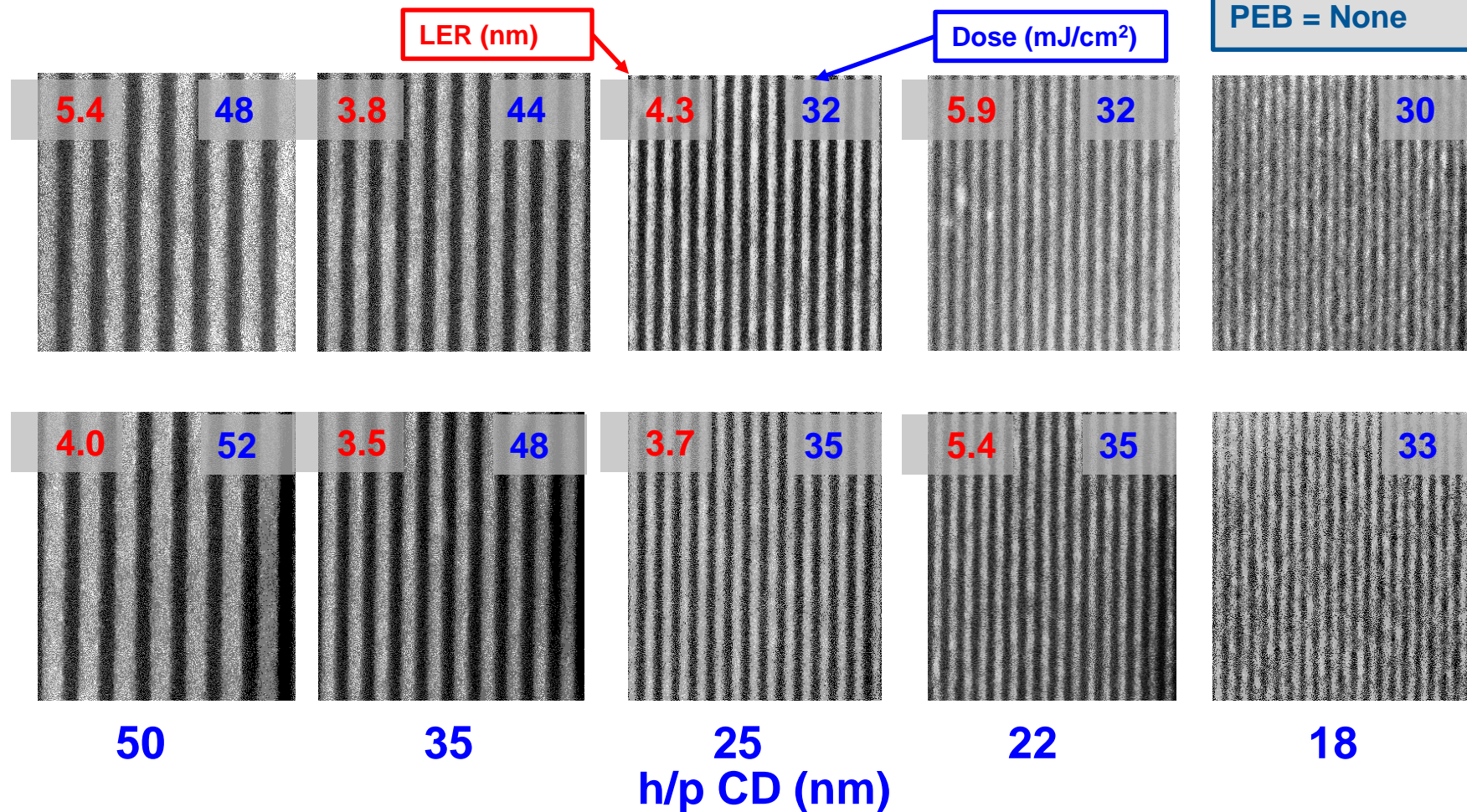




# Cobalt – Imaging at PSI



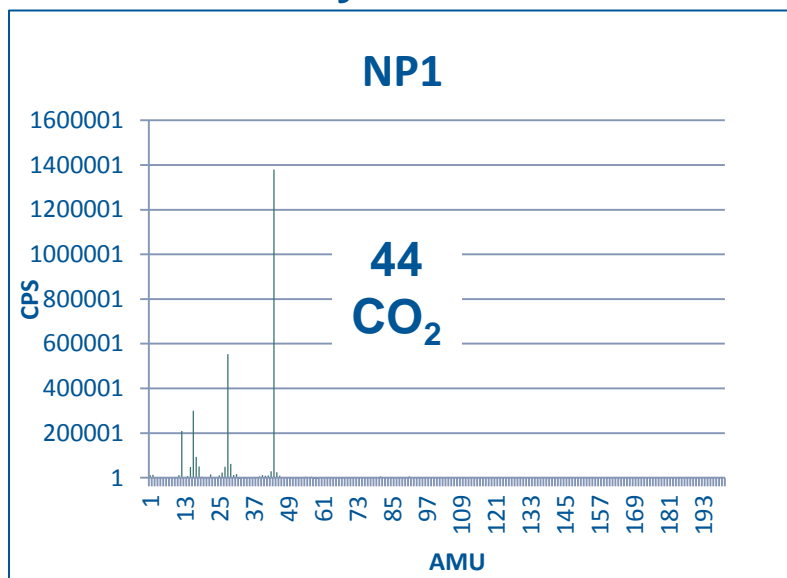
Dev. = MEK/15s  
Thickness = 29nm  
PAB = 90°/60s  
PEB = None





# BTP[Co(bpy)(ox)<sub>2</sub>] Shelf-Life and Outgassing

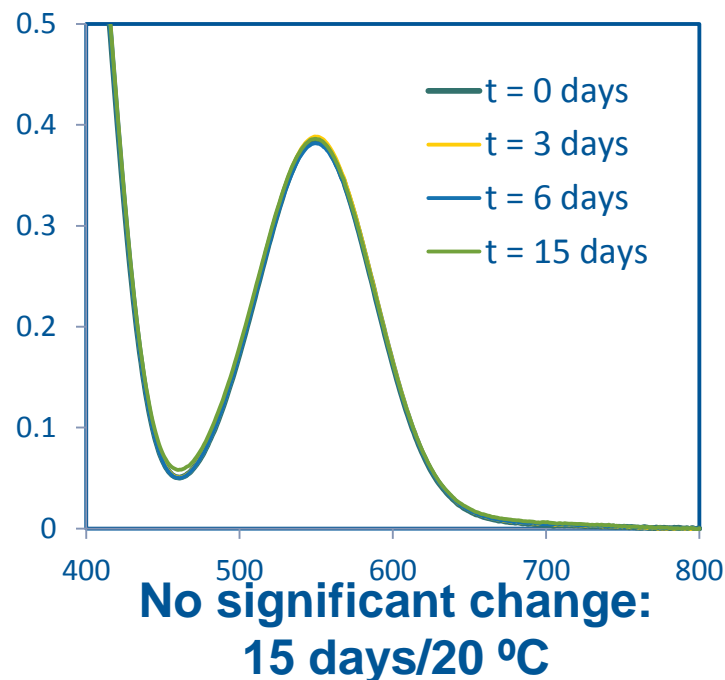
Passes Outgassing Tests  
by ~2X



CO<sub>2</sub> (m/e = 44)  
is the largest peak

Witness plate is underway.

1% solution BTP[Co(ox)<sub>2</sub>(bpy)]  
in 66/33 ethyl lactate/CH<sub>3</sub>CN.  
Absorption vs. wavelength





# Metal-Organic resist



- Manufacturing consideration
  - Shelf-life: very good
  - Low sensitivity to out of band radiation
  - Low outgassing



# Next step



- Enable the supply chain to adopt the new materials
  - Establish stable baseline, understand mechanism.
  - Outgas study, shelf-life characterization, fullfiled exposure are steps towards this goal
  - Involves supply chain players



# Summary



- In last few years SEMATECH has been working on pathfinding of novel metal-based resist systems
- Efforts are being undertaken to evaluate identified baseline resist in novel space for compatibility with high volume manufacturing
- Transition to full-field lithographic characterization is underway for nanoparticle resist.
- SEMAETCH is actively involved with supply chain to enable them to adopt the early technology for further improvement.



# Acknowledgement



- IMEC: for their support for NXE3100 exposure
- INTEL: Marie Krysak for sharing shelf life data for nanoparticle resist
- University of Arizona( Reyes Sierra) : For EHS study of the nanoparticles under SEMATECH sponsorship
- SUNY, New Paltz: Dan Freedman and his group: for oxalate work under SEMAETCH sponsorship
- SEMATECH: For sponsoring this work